

Reconnaissance Evaluation of Platinum -Group Elements in Selected Precambrian Rocks of the, Western Upper Peninsula, Michigan

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Abstract

The abundance of platinum and palladium was determined in selected Precambrian rocks exposed in the western Upper Peninsula of Michigan. Mafic to ultramafic igneous rocks were emphasized because of their higher potential to host platinum-group element mineral resources. No highly anomalous platinum or palladium were indicated from 58 samples collected throughout the western Upper Peninsula. Since anomalous concentrations and deposits of platinum-group elements are expected to occur in difficult to detect zones, it would have been surprising if a significant anomaly would have been located by this study. The layered mafic Kiernan sills in Iron County should be tested by further sampling and systematic stratigraphic drilling.

Introduction

Platinum-group elements (PGE) are essential to the United States industry because of their catalytic properties and electrical conductivity (Page and others, 1973). PGE are considered to be strategic metals as the United States is dependent on foreign sources for over 98 percent of its consumed PGE. The PGE consist of platinum (Pt), palladium (Pd), iridium, osmium, rhodium, and ruthenium. Pt and Pd are the most abundant of these elements.

This is a report of a reconnaissance investigation of the abundance of PGE in selected rocks of Precambrian age exposed in the western Upper Peninsula of Michigan. These data and a survey of the literature with respect to likely locations of PGE ore deposits are a first attempt to characterize PGE in rocks of this area. The only way to truly test the PGE potential of poorly exposed rock is by stratigraphic/systematic drilling. An outgrowth of this project has resulted in a proposed chronology of mafic intrusions of Marquette County by Baxter and Bornhorst (1989).

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the GLMD and reviewed a draft of this report. A final contract report was submitted in 1988 but open filing was delayed in the hope of including additional geochemical data. Unfortunately, these data were not ready to be included in this report.

Procedures

Initially, a review of the literature relevant to anomalous PGE occurrences and deposits was undertaken. Approximately six weeks was devoted to this review but only a small summary of the effort is herein reported. The knowledge gained through the literature review, published geologic maps and literature on the Precambrian rocks of the western Upper Peninsula resulted in the selection of areas for possible sampling localities. Emphasis was placed on mafic/ultramafic intrusions as these rock types are the primary hosts for PGE. Preliminary samples were collected and analyzed for PGE and studied in hand specimen and thin section. Additional reconnaissance samples were collected since the preliminary samples did not yield anomalous data. These additional samples were analyzed for PGE and studied in hand specimen and thin section. Many of the preliminary and additional samples were analyzed for S, Ni, Cu, and Cr. This report is an evaluation of the data in light of published literature, with recommendations for further work, and conclusions with respect to PGE potential of the western Upper Peninsula of Michigan.

A total of 17 man days were spent in the field collecting samples for laboratory study. During this time, 120 samples were collected, about one-half of which were analyzed as described below.

Analytical Procedures

Platinum, palladium, and gold were analyzed by lead fire assay of 20 gram samples followed by determination of concentrations by direct current plasma emission spectrometry. Detection limits are 10 ppb Pt, 2 ppb Pd and 2 ppb Au (gold). Rock samples were analyzed by Nuclear Activation Services, Inc., Ann Arbor, Michigan. Selenium was determined by graphite furnace atomic absorption by Nuclear Activation Services. Detection limit is 0.1 ppm Se. The concentrations of sulfur, nickel, copper, and chromium were determined by T. J. Bornhorst using X-ray fluorescence and following procedures modified from Rose and others (1986). Detection limits for these elements are 20 ppm S and 5 ppm Ni, Cu, and Cr.

A total of 58 samples were analyzed for Pt, Pd, and Au and 4 samples for Sc. Samples with more abundant sulfides or opaque minerals were especially targeted for analysis. Forty-two samples were analyzed for S, Ni, Cu, and Cr. About 50 thin sections were prepared at Michigan Tech for petrography analysis.

Geological Environments of PGE Dominant Deposits

There are three major geological environments of PGE dominant ore deposits: Merensky-type, hydrothermal, and placer (Naldrett, 1981).

Merensky-type

Merensky-type deposits occur in large bodies of dominantly mafic intrusive rocks emplaced in a stable continental setting. This type deposit includes the Bushveld Complex of South Africa, the Stillwater Complex of Montana, and the Lac des Iles complex of western Ontario. These deposits, in particular the Bushveld Complex, are the most important source of PGE. Ore horizons are less than 3 m thick in layered intrusions and contain scattered sulfides and perhaps chromite with grades ranging from 3 to 20 ppm PGE (Naldrett, 1981).

The Bushveld Complex is a large layered mafic to ultramafic intrusion consisting of four main zones: the lower zone mostly composed of harzburgites and bronzitites; the critical zone composed of bronzitites, anorthosites, norites, and layers of chromite; the main zone composed of gabbros, norites, and anorthosites; and the upper zone composed of magnetite gabbros, troctolites, olivine diorites and layers of magnetite (Naldrett, 1981; Von Gruenewaldt, 1979). PGE mineralization occurs in the Merensky Reef, the UG 2 chromitite layer, the Platreef, and discordant dunite pipes. The Merensky Reef is a coarse-grained pegmatoidal feldspathic pyroxenitic unit (Vermaak, 1976) with PGE concentrated in the vicinity of two thin chromitite layers, 2 to 3 mm thick. The mineralization of the Platreef is associated with a zone of sulfide blebs and stringers (Naldrett, 1981).

The Stillwater Complex is a layered succession of mafic and ultramafic rocks (Todd and others, 1982). PGE mineralization is associated with sulfide in the basal portion of the Banded Zone. The Banded Zone consists of norite and gabbro - norite with minor anorthosite, troctolite and gabbro. The mineralized zone is 1 to 3 m thick and has been traced for 40 km. It is characterized by 0.5 to 1 volume percent sulfides (Todd and others, 1982). The PGE mineralization is related to double-diffusive convective mixing of two magmas which resulted in the formation of immiscible sulfide liquid (Irvine and others, 1983). PGE are strongly partitioned into the immiscible sulfide liquids (Campbell and Barnes, 1984).

The Lac de Iles complex consists of ultramafic and gabbroic parts (Talkington and Watkinson, 1984). PGE are associated with disseminated sulfides in layered cumulates of gabbro (dominant), norite, proxenite, and anorthosite (Watkinson and Dunning, 1979). The highest PGE values are associated with original pyroxene rocks, now amphibolites. Talkington and Watkinson (1984) proposed that PGE are first concentrated in immiscible sulfide liquids and later concentrated by hydrothermal processes during either ductile alteration by magmatic fluids and/or metamorphism.

In a broad sense, layered or zoned intrusions of mafic to ultramafic rocks have potential for PGE dominated mineralization. The mineralization would probably be associated with disseminated sulfides and/or chromite. The zone of mineralization will probably be relatively thin resulting in difficulty of discovery or geochemical detection. Exploration programs, such as those in Finland, have found the best success by using stratigraphic drilling.

Hydrothermal Deposits

The New Rambler deposit, Wyoming, consists of Pt and Pd in close association with irregular pods of copper and iron sulfides hosted in

altered diorite and gabbro. The ore deposit occurs along a major shear zone (McCallum and others, 1976). The ores are related to hydrothermal processes.

Placer Deposits

Deposits of PGE have been mined from eluvial and alluvial sediments. Most such deposits are in spatial association with ultramafic rocks which are enriched in PGE (PGE enrichment is often associated with chromite) (Naldrett, 1981).

Geological Environments of By-Product PGE Mineralization

PGE are also recovered as a by-product in the processing of other types of ore deposits. Most notably Ni-Cu sulfide deposits can contain significant amounts of PGE. PGE are concentrated in thin zones within the Kupferschiefer copper deposits of Europe.

Ni-Cu Dominant Deposits

Anomalous PGE are associated with Ni-Cu deposits of the Sudbury district, Ontario, the Duluth Complex, Minnesota and Kambalda district, Western Australia. The Sudbury complex is a large layered mafic intrusion with PGE associated with pyrrhotite-pentlandite-chalcopyrite-pyrite-magnetite ore (Naldrett, 1981). In the Duluth Complex PGE are associated with sulfides near the base of the complex. Sulfur was probably derived from the underlying sulfide facies iron formation (Mainwaring and Naldrett, 1977). At Kambalda, Ni sulfide deposits occur in association with komatiites. The deposits are interpreted as related to immiscible sulfides (Naldrett and Cabri, 1976).

Kupferschiefer

The Kupferschiefer is known for economic concentrations of Cu in sandstone, black shale, and dolomite. In Poland, Au and PGE occur in a few centimeter thick layer at the base of the black shale (Kucha, 1982). The relatively abundant PGE are interpreted as due to auto oxidation and desulfurization of organic matter.

Geochemistry of PGE

The geochemistry of PGE is complex. With respect to those deposits in mafic to ultramafic igneous complexes, the concentration in rocks above or below the deposit can be either enriched or depleted as compared to the original (parent) magma composition. Thus, the abundance of PGE in a given sample of rock may or may not indicate the potential of the rock body for mineral resources. Nevertheless, regardless of such shortcomings, a sampling program was initiated and the abundance of PGE were determined for a variety of rocks from Proterozoic Archaean granitoid* and gneiss throughout the western Upper Peninsula. Since anomalous amounts of PGE are often associated with either sulfides (Ni, Cu, and Fe) and chromite many of the samples analyzed for PGE were also analyzed for S, Ni, Cu, and Cr.

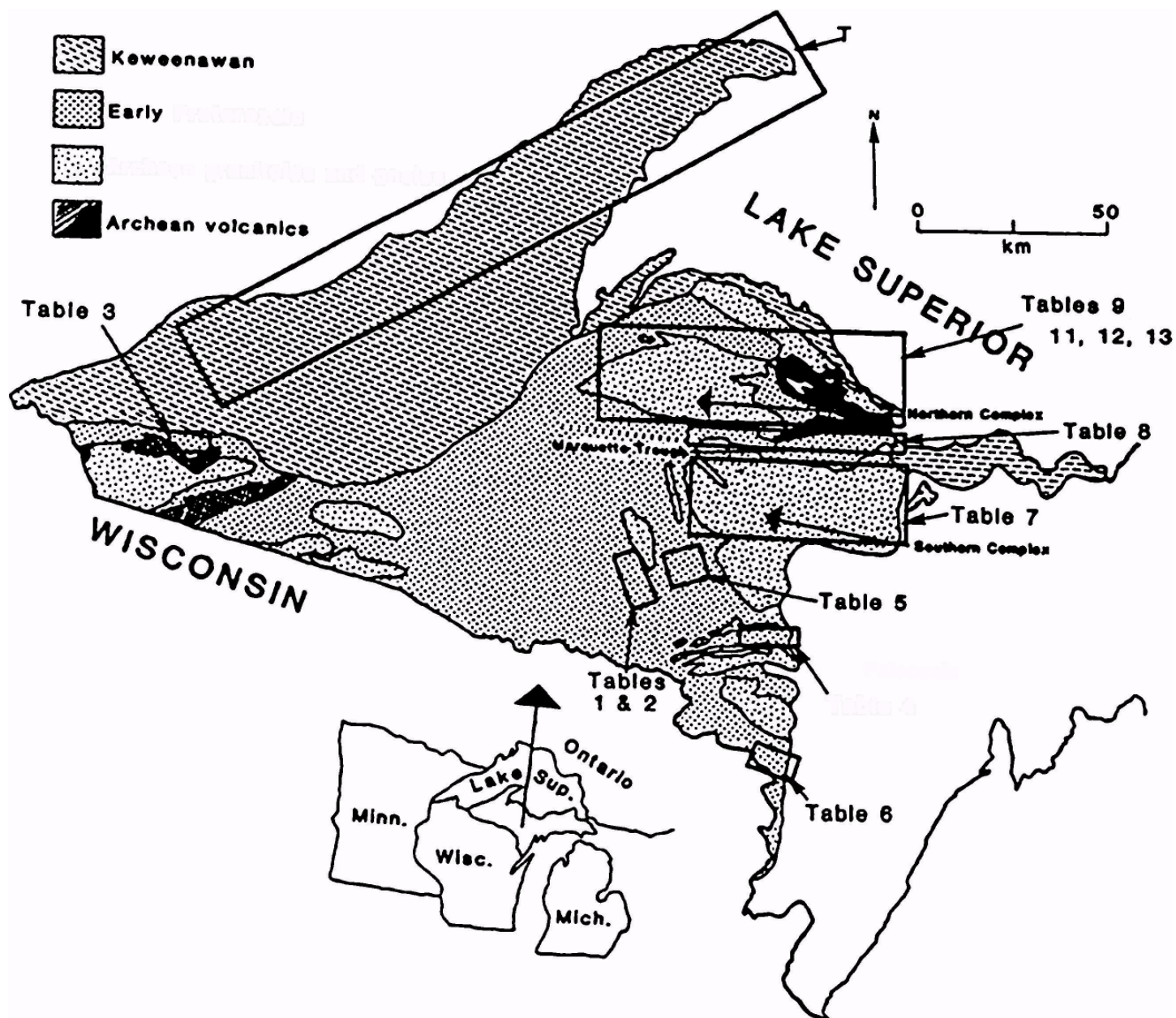


Figure 1. Generalized geologic Map of the western Northern Peninsula of Michigan showing areas sampled in this study. Tables refer to data.

Pi and Pd are usually the most abundant of the PGE. Their abundance varies between rock type and tectonic environments (Crockel, 1979). In unmineralized rock, Pi content is typically less than 50 ppb and Pd is less than 25 ppb. Basalts generally contain less than 10 ppb Pd. The PGE contents of initial magmas of the Stillwater Complex are Pi, 12 ppb and Pd, 55 ppb (Crocket, 1979). In general, there is a progressive decrease in the PGE content in sulfur poor rocks towards more silicic compositions. Sulfur saturation during differentiation can substantially effect these trends since PGE are strongly partitioned into sulfur-rich liquids. High PGE contents are associated with chromite (Crockel, 1979) and magmatic sulfides (Campbell and Barnes, 1984).

Eckstrand (1987; personal communication) has shown that PGE dominated deposits can be distinguished by means of selenium/sulfur ratios. Selenium/sulfur ratios of greater than 250 to 300 X 10⁶ indicate mantle derived source of sulfur and a higher

potential for PGE deposits. A few data on Se were collected as part of this project.

Sampling Strategy

Since the known occurrences of anomalous and ore grade PGE are preferentially located in intrusive rocks of mafic to ultramafic composition, it was logical to focus this reconnaissance evaluation on these rock types. All mafic intrusive rocks in the western Upper Peninsula were considered as possible sampling targets. Due to its relatively large size and layered nature the Kiernan sill was of special interest. A variety of other mafic intrusive bodies of varying shapes and sizes were sampled. In addition, 3 different peridotite bodies, the rocks of the native copper district of the Keweenaw Peninsula,

black shale related Cu ore from the White Pine Mine, and ore from the Ropes Gold Mine were tested.

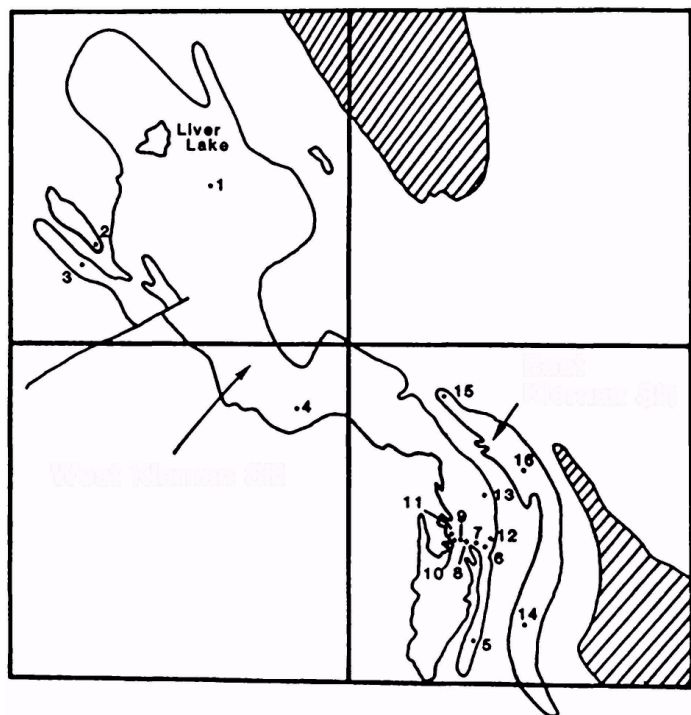


Figure 2. Generalized geologic map of the southeast part of Iron County showing the location of the Kiernan sills. Numbers refer to Report Numbers in Table 1 and 2.

Results

The chemical data for this study are given in Tables 1 thru 14, organized by geography and geology. The distribution of samples collected in the western Upper Peninsula is shown on Figure 1. None of the samples yielded anomalous PGE concentrations as compared to data from the literature for unmineralized rocks. Most of the samples contained Pt, Pd and Au at concentrations less than the detection limit of 10, 2, and 2 ppb respectively.

Kiernan Sills

The Kiernan sills (west and east) are mafic bodies which intrude into the Hemlock Volcanics in eastern Iron County (Fig. 2). The west sill is the larger of the two and is a maximum of about 2 km thick with a strike length of about 19 km. It is grossly layered (differentiated) and consists of a basal ultramafic zone successively overlain by a normal gabbroic zone, transitional and granophyric zones, and diabasic (chilled) zone (Bayley, 1959a and b; Gair and Wier, 1956; Wier, 1967; Fox, 1983). Representatives of the various zones were sampled and also a magnetite-rich differentiate described by Weir (1967). Most samples contained Pt and Pd less than the detection limit. Two Cr rich samples yielded detectable Pd of 9 and 2 ppb (Table 1A). Sample No. 1 is an ultramafic rock from the Liver Lake area and No. 5 is from the basal ultramafic zone in the southernmost part of the sill (Fig. 2). Additional samples should be collected in the Liver Lake area for analysis from all known outcrops. However, the sill is poorly exposed in the Liver Lake area.

The east Kiernan sill consists of gabbro with very small and widely scattered blebs of sulfide. All three samples had detectable Pd and two had detectable Au (Table 2A).

Gogebic County

Prinz (1967) mapped a number of diabase and gabbro sills and dikes in the eastern Gogebic iron range. One of them was described as magnetite-rich. The magnetite-rich gabbro did not have detectable Pt nor Pd. Diabase at Wolf Mountain (Trent, 1973) contains anomalous Cu and detectable Pd at 4 ppb (Table 3A).

Dickinson County

The Sturgeon-Skunk River sill was mapped by James and others (1961) as diabase and gabbro with a strike length of over 14 km with a typical width of 0.2 km except in the far eastern end where it thickens to 1.3 km. One sample had Pt and Pd below the detection limits (Table 4A).

Snider (1977) described an ultramafic body in north central Dickinson County. This is a serpentinized peridotite with a outcrop width of about 1 km and length of about 6 km. One sample analyzed had detectable Pd of 2 ppb (Table 5A).

The Sturgeon Falls sill is located in the southern part of Dickinson County and consists of serpentine at the base overlain by gabbro (Schulz, 1984). The serpentinite had Pt and Pd below the detection limit whereas a sample of gabbro had Pt below the detection limit and Pd of 2 ppb (Table 6A).

Southern Complex

Mafic dikes intrude Archean granitoid rocks of the southern complex (Gair and Thaden, 1968; Cannon, 1974, 1975; Gair, 1975). Sample No. 26 yielded the highest Pt and Pd values of any rock analyzed in this study of 20 and 13 ppb, respectively (Table 7 A). This sample is from a 20 m wide N-S trending dike just north of Powell Lake in the Sands quadrangle (Gair and Thaden, 1968). There is nothing obvious in the sample which suggests a higher PGE concentration than other similar rocks sampled.

Marquette Trough

There are numerous dikes and sills which intrude Early Proterozoic sediments of the Marquette Range Supergroup (Gair and Thaden, 1968; Puffelt, 1974; Clark and others, 1975; Simmons, 1974; Klasner and Cannon, 1978; Cannon and Klasner, 1977; Cannon, 1974). These bodies are typically gabbro and correlated as Early Proterozoic in age (Michigan Formation lime) (Cannon, 1974; Baxter and Bornhorst, 1988). Nine samples have Pt below the detection limit and all but two have Pd below the detection limit, those two contain Pd of 2 ppb (Table 8A).

Northern Complex

Mafic intrusive rocks cut Archean rocks of the Herman area of the northern complex (Turner, 1973; Bodwell, 1972). Only one sample had detectable Pd of 2 ppb (Table 9A).

The Yellow Dog Peridotite has been studied by Klasner and others (1979) and Morris (1973). It is located in the northern part of the northern complex where it is surrounded by unconsolidated

Pleistocene glacial sediments. Its extent is unknown although geophysical surveys by Klasner and others (1979) indicate the possibility of multiple dikes over a strike length of 20 kilometers. Klasner and others (1979) suggest that this may be an igneous complex of early Keweenaw age. They noted the occurrence of 1 to 2 percent pyrrhotite, pentlandite, and chalcopyrite and concluded that this body should be investigated further for possible mineralization.

For this study six samples were analyzed (Table 10A). The exposed peridotite appears to contain about 10 ppb Pt and about 5 to 6 ppb Pd. On a world wide basis these concentrations are not anomalous but as compared to most of those samples analyzed in this study the Yellow Dog Peridotite has higher Pt and Pd.

The Deer Lake Peridotite and spatially associated Ropes Gold Mine have been described by Rossell (1983), Bornhorst and others (1986), and Brozdowski (1989). The peridotite contains less than detectable Pt and Pd whereas gold ore from the Ropes Gold Mine contains detectable Pd at 3 ppb (Table 11A).

The Archean granitoid rocks of the north one-half of the Marquette 7 1/2 minute quadrangle arc intruded by numerous thin mafic dikes (Gair and Thaden, 1968). No samples yielded detectable Pt or Pd but three of them did yield Au of 4 to 5 ppb (Table 12A).

Two miscellaneous samples include one from the waste-rock piles of the Champion iron mine. High grade yellow sulfides did not yield detectable Pt or Pd but did contain 950 ppb Au. A N-S trending Keweenaw dike from the Reany Lake area (MacLellan and Bornhorst, 1988) had Pt and Pd below detection limits (Table 13A).

Keweenaw Peninsula and Vicinity

The geology and native copper mineral deposits are described by White (1968). A sample from the | Greenstone Flow, native copper mineralized Kingston 1 Conglomerate, and late-stage Cu-arsenide veins from the Mohawk Mine had Pt and Pd below the detection limits (Table 14A). Three samples from the White Pine Mine (Ensign and others, 1968) had Pd of 4 to 5 ppb and two samples indicate 2 ppb Au (Table 14A).

Selenium Data

Eckstrand (1987; personal communication) has suggested that the Se/S ratio can be used as an indicator of PGE potential. Those rocks with "mantle" Se/S ratios (greater than 250 to 300 X 10⁶) are considered to be greater than average PGE targets for exploration. To be effective one should be able to determine Se at the 50 ppb level. This can be accomplished by atomic absorption using a hydride collection process on solutions obtained by ordinary dissolution. Since hydride collection process is not currently developed for analysis of geological materials at Michigan Technological University, four samples were submitted elsewhere for analysis with a 100 ppb detection limit and reported to an even 100 ppb (0.1 ppm) (Table 15).

These data are inconclusive for the potential of the west Kiernan sill whereas they indicate favorable environment for the east Kiernan sill. The low Se/S ratio for the north central Dickinson County peridotite is unfavorable. The marginal Se/S ratio for the Yellow Dog Peridotite is inconclusive.

Bivariate Geochemical Relationships

Considering all of the geochemical data presented in this report, as a whole, the only combination of elements to show an obvious relationship is Ni and Cr. These two elements show a positive correlation. Although the data are too few to be statistically significant, Pt and Pd may be positively correlated with a Pt/Pd ratio of about 2:1. Based on bivariate plots, Pd has a very poorly defined positive relationship with Ni, Cr, and Au, however, none of these are statistically significant.

Recommendation For Further Work

There are numerous mafic intrusions in the western Upper Peninsula which could not be studied during this limited investigation. In particular, the Peavy Pond complex should be evaluated. Even for those bodies described in this report contain many surface exposures which were not sampled but should be. All of the rock bodies studied are not completely exposed and hence there is a high probability that a mineralized horizon could be present but not available for sampling. For example, the northern part of the west Kiernan sill (Liver Lake area) and the Yellow Dog Peridotite are poorly exposed, but these areas, at least, had detectable Pt or Pd, although not especially anomalous with respect to typical mafic rocks. There are two obvious approaches to resolving this problem. Geophysical surveys could be used to locate potentially favorable buried horizons which could then be drilled. A remote geochemical method such as the Se/S ratio method, developed by Eckstrand, could be used to further test the PGE potential of mafic and ultramafic rocks of the western Upper Peninsula. For the layered intrusions the best method to test their PGE potential is systematic stratigraphic drilling.

Conclusions

No highly anomalous Pt or Pd values were indicated from 58 samples collected throughout the western Upper Peninsula. Although initially, this may seem to indicate negative potential, however, it should be clear to the reader that, as a reconnaissance study this is the first attempt to characterize the PGE abundances in rocks of the western Upper Peninsula. Since anomalous concentrations and deposits of PGE can occur in relatively thin zones and require chemical analysis for detection, it would have almost been surprising if a significant anomaly would have been located by this study.

The potential of the western Upper Peninsula for discovery of PGE resources remains open. This report serves the purpose of providing some indications of potential in the Upper Peninsula for future testing.

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